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Mass Balance Modeling of DDT Dynamics in Lakes Michigan and Superior

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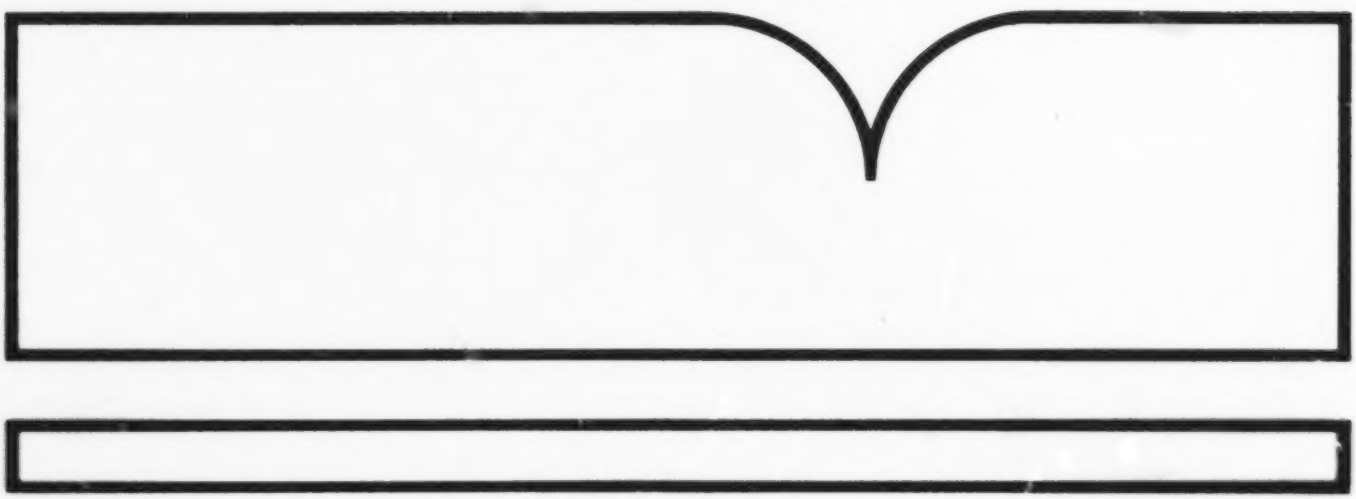

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Mass Balance Modeling of DDT Dynamics in Lakes Michigan and Superior

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■ A retrospective analysis of DDT dynamics subsequent to the imposition of a ban on DDT use in 1969 was conducted for Lakes Michigan and Superior. Trends in the available data indicate that DDT levels in both lakes declined at greater rates than were expected on the basis of hydraulic detention times and the degradation rate for DDT in the environment. Under the given assumptions, settling of particulate DDT from the water column was found to be the major loss process of DDT for both lakes. Particulate settling was responsible for 61–95% of the observed DDT loss rate in Lake Michigan. Degradation and hydraulic washout were responsible for 3–35% and 2–4%, respectively. Results for Lake Superior were comparable. These ranges corresponded to results for sensitivity analyses to variations in external DDT loads, partition coefficients, and degradation half-times. Results for apparent net particulate settling velocities for DDT were consistent with analogous results for phosphorus, phytoplankton, and plutonium from independent studies.

Introduction

The organochlorine pesticide DDT was one of the first synthetic chemicals to be produced in large quantities and to be widely dispersed in the environment. For more than 20 years, beginning in the late 1940s, DDT was widely used in the Great Lakes region, especially in the Lake Michigan basin. In the late 1960s, increased environmental awareness, supported by a growing body of scientific evidence, led to the discovery of widespread distribution of DDT throughout the Great Lakes ecosystem (*1*). It was found that DDT had been transported to the lakes by municipal and industrial waste discharges, tributaries, land runoff, and atmospheric deposition subsequent to aerial spraying. The persistent chemical structure of DDT and its capacity for accumulation in fish tissue caused grave public concern. The Lake Michigan Interstate Pesticide Committee (*2*) found that levels of DDT in sport and commercially valuable fish exceeded the action level established by the Food and Drug Administration for human consumption.

A chronology of political responses to the DDT problem was developed by Lowrance (*3*). In 1969, the U.S. Court of Appeals directed the U.S. Department of Agriculture to ban the use of DDT in the Great Lakes Basin. The following year, the U.S. Environmental Protection Agency (EPA) was established and given authority to regulate pesticides. Under an order from the same court in 1970, the EPA imposed a temporary ban on DDT in the form of a cancellation of DDT registration as an approved pesticide. Finally, in 1972, EPA ordered full suspension of DDT use for agricultural and other non-health-related purposes.

Since the DDT ban, there have been declines in DDT residues in fish and gull populations throughout the Great Lakes (*4*). Declines in DDT in herring gull eggs were reported for both Lakes Michigan and Superior, although the declines were less substantial for Lake Superior. More information is available for DDT on Lake Michigan than for any of the other Great Lakes (*1*, *5–7*). Konasewich et al. (*6*) reported that DDT concentrations in fish in Lake Michigan have decreased steadily to approximately 10–25% of 1969 concentration values. The available data for Lake Superior indicated the same trend.

Table I. DDT Residues in Coregonid Fishes of Lakes Michigan and Superior, 1969–1978

	Lake Michigan[a]		Lake Superior	
year	no. of fish	total DDT, μg/g[b]	no. of fish	total DDT, μg/g
1969	120	9.94 (0.33)	5	1.81[c]
1970	28	9.87 (1.44)	150	1.58[d]
1971	60	6.24 (1.13)	15	1.59[d]
1972	120	4.33 (0.48)		
1973	160	2.09 (0.26)		
1974	110	1.33 (0.14)	26	0.45[e]
1975	170	1.27 (0.20)	31	0.407[e]
1976	110	0.90 (0.06)		
1977				
1978	100	0.81 (0.07)		

[a] Reference 42. [b] Concentrations in whole fish, wet weight, with 95% confidence interval in parentheses. [c] Reference 43. [d] Reference 44. [e] Reference 45.

Since DDT is only one of many different persistent organochlorine contaminants in the environment, it is important to understand the processes controlling its fate, transport, and distribution. DDT is a hydrophobic compound with low water solubility. Its solubility in lipids is much higher. This property leads to the accumulation of DDT in various biotic compartments, especially in fish tissue. In addition, DDT also tends to adsorb strongly to particulate materials in the water column and sediments. The chemical structure of DDT is such that it is extremely resistant to degradation in the environment, and hence, it tends to persist for long periods of time.

This study was an attempt to use the available data for Lakes Michigan and Superior for a retrospective analysis of DDT dynamics subsequent to the imposition of the ban in 1969. DDT was unique in that it was the only contaminant added to the Great Lakes on a massive scale whose use was abruptly terminated. Mass balance studies were conducted to identify the principal processes responsible for the observed declines in DDT levels. The primary purpose of this study was to understand these processes by testing various hypotheses and comparing results to existing information from independent studies.

Data

The available data for DDT in the Great Lakes are not sufficient to define the time histories of concentrations in the water column and sediments or of external loads from tributary and atmospheric sources. A major obstacle to the acquisition of reliable monitoring data has been the lack of development of sufficiently sensitive and accurate analytical methods for DDT. Attempts to measure levels of DDT in water and seston, for example, have frequently resulted in nondetection or in detection of only trace quantities (*8*).

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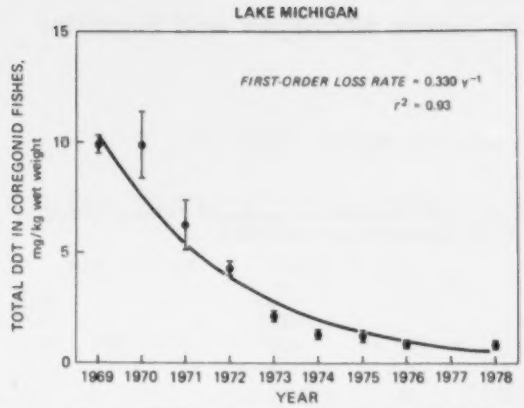

Figure 1. Observed DDT levels in coregonid fishes in Lake Michigan.

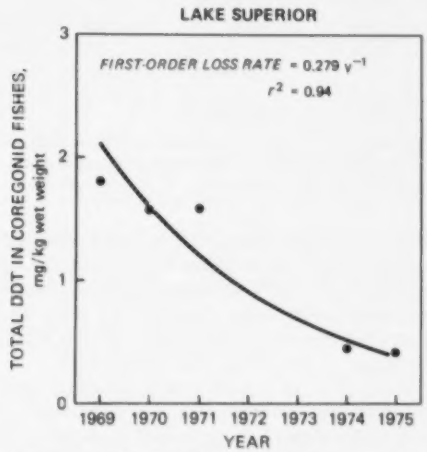

Figure 2. Observed DDT levels in coregonid fishes in Lake Superior.

The longest continuous monitoring effort for DDT on the Great Lakes has been conducted by the U.S. Fish and Wildlife Service (*6*). Since 1969, DDT levels have been measured in several major groups of fishes in Lake Michigan. Similar data, although somewhat more limited, have also been acquired by several different investigators on Lake Superior. Table I contains the available data for coregonid fishes from both lakes over the period 1969–1978. Coregonid fishes consist primarily of lake herring and their relatives the bloater chubs. Data for the coregonid group constitute the most complete record of DDT levels in Lake Michigan over the 9-year period following the DDT ban. Throughout this paper, DDT is considered to be total DDT, which includes DDT and the sum of its degradation products DDE and TDE.

Trends in DDT Levels

The coregonid fish data for Lakes Michigan and Superior are illustrated in Figures 1 and 2, respectively. During the periods of observation, DDT levels declined substantially in both lakes. The data conformed well to first-order loss rate kinetics. The illustrated loss trajectories were based on least-squares fits and corresponded to half-times of 2.1 years for Lake Michigan and 2.5 years for Lake Superior. Levels in each lake showed sharp declines shortly after the discontinued use of DDT. These trends were inconsistent with the loss rates that were expected on the basis of hydraulic detention times and the degradation rate for DDT in the environment. The hydraulic detention times for Lakes Michigan and Superior are 69

DDT CONCEPTUAL MASS BALANCE MODEL

$$\frac{dC}{dt} = \text{External load} - \left\{\begin{matrix}\text{Hydraulic}\\ \text{washout}\end{matrix}\right\} - \left\{\begin{matrix}\text{Settling of par}\\ \text{ticulate phase}\end{matrix}\right\} - \left\{\begin{matrix}\text{Degradation of}\\ \text{dissolved phase}\end{matrix}\right\}$$

Assumptions:

dC/dt is proportional to change in DDT concentration in Coregonid fishes.

Net settling losses can be parameterized by an apparent settling velocity on the particulate phase.

DDT degradation can be parameterized by a pseudo-first-order mechanism on the dissolved phase.

Vapor phase mass fluxes are negligible.

The whole lake is a single mixed reactor.

Annual average time scale.

Figure 3. Summary of conceptual components in DDT mass balance model.

years (*9*) and 177 years (*10*), respectively, and the half-time for degradation of DDT in various aquatic environments has been estimated to range between 8 and 15 years (*11–13*). It was apparent that the DDT trends in Lakes Michigan and Superior were controlled by factors other than simple hydraulic washout and degradation.

Conceptual Approach to Mass Balance Modeling

Because of the paucity of data, the modeling approach was based on the minimum number of assumptions required to describe DDT dynamics in the lakes. The assumptions and rationale used for spatial and temporal scales were the same as those used by Chapra and Sonzogni (*10*) for modeling total phosphorus concentration in the Great Lakes. With regard to spatial scale, both lakes were considered to be completely mixed reactor systems. There was no spatial segmentation in the horizontal or vertical directions. With regard to temporal scale, data and model output were intended to represent annual average values.

The processes included in the model and the principal assumptions are contained in Figure 3. Degradation of DDT in the environment can occur due to hydrolysis, photolysis, and microbial degradation (*14, 15*). The effects of these processes have been aggregated into a pseudo-first-order loss mechanism for the dissolved phase. This simplification ignored the possible effect of particulates on the overall degradation process. It has been shown that DDT strongly adsorbs to particulate materials, including plankton in the water column (*16–20*). The subsequent settling of these materials out of the water column can constitute an important loss process. These effects have been aggregated into a single net settling mechanism expressed in terms of an apparent net settling velocity. This velocity corresponded to the net flux of DDT from the water column to the sediment.

It was assumed that vapor-phase mass flux of DDT was not significant. It is conceivable that vapor-phase mass flux could constitute either a source or a sink for DDT in the water column. The available data are not sufficient to establish an accurate time history of this flux if, indeed, such a flux existed in the lakes during the period of observation. Below, available data are analyzed, and order of magnitude estimates are developed for DDT vapor-phase gradients bounding the period of interest.

An important assumption was that water column concentrations of DDT were proportional to observed DDT levels in fish. This assumption was necessary because of the paucity of historical data for DDT water column concentrations available for comparison with model output. Most of the evidence in the literature supports this assumption, although there is some disagreement on the relative importance of the actual uptake pathways. Jar-

vinen et al. (*21*) found that water uptake of DDT by fish was more important than dietary uptake in determining total DDT tissue residue. They concluded that DDT levels in fish were good indicators of water concentrations. Hamelink et al. (*22*) proposed that DDT levels in fish were controlled primarily by equilibrium partitioning with water column concentrations. Hamelink and Waybrant (*23*) supported this hypothesis using results from a large-scale ecosystem study. Macek and Korn (*24*), however, contended that the food chain was a major source of DDT fish residues in natural waters.

So that the basis for the assumption that DDT levels in fish were proportional to water column concentrations could be strengthened, only DDT data for coregonid fishes were used. Data for bloater chubs (*Coregonus hoyi*) and deep-water ciscoes (*Coregonus johannae*) were used from Lakes Michigan and Superior, respectively. These species are closely related in terms of taxonomy, biology, and behavior. Coregonid fish are part of a food chain that is principally pelagic. Generally, coregonids in the early life stages feed on zooplankton, and in the later life stages feed on *Mysis* and *Pontoporeia* (*25, 26*). It has been shown that levels of DDT and other persistent chlorinated hydrocarbons in pelagic biota are controlled by equilibrium partitioning with water column concentrations (27–29). Thus, the principal coregonid diet should contain DDT levels that are controlled by ambient DDT concentrations. Armstrong (*30*) has hypothesized that biota in the pelagic dietary pathway should be expected to show rapid responses to changes in water column concentrations of persistent chlorinated hydrocarbons and that biota in the benthic dietary pathway should be expected to show much slower responses. This is because adsorption to particulate material in the water column, and subsequent settling, can constitute a loss process for the water column. There is no such equivalent loss process for the benthic compartment. In essence, the validity of the present results does not depend on the actual uptake pathway, or on the absolute accuracy of the transformation from DDT levels in fish to DDT water column concentrations. It is sufficient to establish that the water and fish levels are proportional and then to ensure that the trajectory of the model output for water column concentrations agrees with the trajectory of the DDT levels in the fish.

Model Application

The dynamic mass balance model for DDT was applied in the following form:

$$\frac{dC_T}{dt} = \frac{W}{V} - \frac{Q}{V}C_T - \frac{v_s C_P}{z} - K_D C_D \qquad (1)$$

where C_T = total DDT concentration in the water column (mass/volume), W = external loading rate (mass/time), V = lake volume (volume), Q = water flow-through rate (volume/time), v_s = apparent net settling velocity for particulate DDT (length/time), C_P = particulate DDT concentration (mass/volume), z = lake depth (length), K_D = first-order rate constant for DDT degradation (time^{-1}), and C_D = dissolved DDT concentration (mass/volume). Equation 1 was similar to that used by Schnoor (*31*) to model dieldrin in Coralville Reservoir, the only difference being that biological uptake of DDT was not explicitly considered in this study. The biological fate of DDT, however, was implicitly included in the particulate-phase concentration.

Total DDT was resolved into particulate and dissolved components by using an equilibrium partition relationship with ambient suspended solids concentrations. The fraction of total DDT in the dissolved form was given by (*11, 31*)

$$f = \frac{1}{K_P C_{ss} + 1} \qquad (2)$$

where f = fraction of total DDT in dissolved form, K_P = equilibrium partition coefficient (dimensionless), and C_{ss} = suspended solids concentration (mass of solids/mass of solution).

Table II. Mass Balance Parameters for Lakes Michigan and Superior

parameter	Lake Michigan	Lake Superior
depth, m	85[a]	145[a]
volume, L	4.91×10^{14}[a]	1.19×10^{15}[a]
hydraulic detention time, years	69[b]	177[a]
suspended solids concentration, mg/L	1.0[c]	0.75[d]

[a] Reference 10. [b] Reference 9. [c] Reference 46. [d] Reference 47.

Model results are presented for several different cases, based on different assumptions for the values of external loadings. A base-line value of 5×10^5 was used for the partition coefficient between DDT and suspended solids. This value was consistent with the range of values reported in the literature for partitioning of DDT to plankton and solids (*16–18*). A base-line value of 0.069 year^{-1} was used for the degradation rate constant. This value corresponds to a half-time of 10 years and was consistent with the range of estimates reported in the literature (*11–13*). Results are presented below for the sensitivity of model results to changes in values for the partition coefficient and the degradation rate constant.

Case 1. External Load Equal to Zero for the Period 1969–1978. As a first approximation, it was assumed that the effect of the ban was absolute and instantaneous, beginning in 1969. This assumption was not completely realistic because it has been shown that residual DDT inputs to the Great Lakes still exist from atmospheric sources (*32*); however, the results provided a frame of reference for sensitivity analysis. Since $W = 0$, eq 1 now becomes

$$\frac{dC_T}{dt} = -\frac{Q}{V}C_T - \frac{v_s C_P}{z} - K_D C_D \qquad (3)$$

With $C_D = fC_T$ and $C_P = (1 - f)C_T$, eq 3 can be rewritten as

$$\frac{dC_T}{dt} = -\left[\frac{Q}{V} + \frac{v_s(1-f)}{z} + K_D f\right]C_T \qquad (4)$$

Thus, an overall loss rate coefficient, K_{total}, can be defined as

$$K_{total} = \left[\frac{Q}{V} + \frac{v_s(1-f)}{z} + K_D f\right] \qquad (5)$$

where K_{total} incorporates the effects of the individual loss processes due to hydraulic washout, settling of particulate DDT, and degradation of dissolved DDT. The value of K_{total} is equivalent to the values of the observed whole lake loss rates for DDT in Figures 1 and 2 under the given assumptions.

Setting K_{total} equal to these values and substituting the parameter values from Table II into eq 5, we obtained values of 68.8 and 118 m/year for v_s for Lakes Michigan and Superior, respectively. These values were generally consistent with the range of apparent net settling velocities

determined in independent modeling studies of phosphorus, phytoplankton, and plutonium at the whole system scale in the Great Lakes (*10, 33–37*). These results suggest that DDT losses from the water column in Lakes Michigan and Superior occur by processes similar to those responsible for losses of other constituents. It should be pointed out that the above results did not depend on the transformation of DDT levels in fish to DDT concentrations in the water column. The assumption that external loading was zero allowed the direct equivalence of the observed DDT loss trajectories defined by the fish data to the overall loss rate in the model.

Case 2. External Load Equal to Present Atmospheric Load for the Period 1969–1978. A more realistic approximation of external loading rates was to assume that they were equal to the presently observed rates of total atmospheric deposition. Eisenreich et al. (*5*) have suggested that atmospheric deposition of organic pollutants, especially DDT and PCBs, respresents a substantial if not the major source of loadings to the Great Lakes. They have developed loading estimates for DDT of 0.40 metric tons per annum (mta) to Lake Michigan and 0.58 mta for Lake Superior.

To determine values of v_s for the present case, it was necessary to solve eq 1 directly, since W was nonzero. For provision of data for comparison with model output, the DDT fish levels corresponding to the curve-fitted trajectories in Figures 1 and 2 were transformed to DDT water column concentrations by using a distribution coefficient of 10^6. This value was used because it resulted in transformations that were consistent with the available DDT water column data. For example, a distribution coefficient of 10^6 and a DDT fish level of 10.4 mg/kg in 1969 (Figure 1) correspond to a DDT water column concentration of 10.4 ng/L. The actual reported range of DDT concentrations in the open-water zone of Lake Michigan in 1969 was 1–31 ng/L; however, because of sampling and analytical difficulties, it was estimated that the most likely range was 1–10 ng/L (*2*). Values for the distribution coefficient lower than 10^6 would have corresponded to unrealistically high DDT water column concentrations. In the opposite limit, values higher than 10^6 would have been inconsistent with the range of values for distribution coefficients reported for DDT in fish (*22, 23*). All other parameters were identical with those used in case 1 above. Equation 1 was calibrated to the data by varying the value of v_s until the model ouput matched the transformed concentrations. Operationally, this procedure was equivalent to a least-squares fit of model output to the DDT response trajectories for each lake.

The calibrated values found for v_s were 84.0 m/year for Lake Michigan and 151 m/year for Lake Superior. These values were not substantially different from those found in case 1. The results suggest that despite uncertainties in the magnitudes of external DDT loadings, apparent net settling velocities for particulate DDT were still consistent with those determined for other constituents in the Great Lakes.

Comparison of Results with Independent Studies

Table III contains a detailed comparison of the apparent net particulate settling velocities found for DDT in the present study to the equivalent velocities found for phosphorus, phytoplankton, and plutonium in three independent studies. The DDT velocities were within the ranges of the velocities for these other constituents in both Lakes Michigan and Superior. The principal loss process for phosphorus and plutonium in the Great Lakes is particulate settling. Apart from consumptive and endogenous processes, settling is also the major loss process for phytoplankton. The present results, therefore, suggest that particulate settling is of major importance in the loss of DDT from the water column.

Table III. Comparison of Apparent Net Particulate Settling Velocities for Lakes Michigan and Superior

	settling velocity, m/year		
constituent	Lake Michigan	Lake Superior	Lake Superior / Lake Michigan
phosphorus[a]	24.5	39.2	1.6
phytoplankton[b]	73		
plutonium[c]	210	369	1.76
DDT (case 2, present study)	84.0	151	1.80

[a] Reference 10. Equivalent particulate velocities calculated from velocities for total phosphorus using observed ratios of particulate to total phosphorus from EPA, STORET. [b] Reference 33. [c] Reference 37. Equivalent particulate velocities calculated from velocities for total plutonium using ratios of particulate to total plutonium based on equilibrium partitioning (K_p = 2×10^5, ref 37) and ambient suspended solids concentrations (Table II).

A remarkable observation is the consistency in the ratio of Lake Superior to Lake Michigan apparent net particulate settling velocities for the different constituents among the independent studies (Table III). The definition of an apparent net settling velocity is strictly operational because it is the net result of equivalent downward settling velocity and equivalent upward velocity due to resuspension. Apparent net settling velocities should not be expected to be the same for a given constituent in different lakes. The reason is that apparent net settling is determined not only by gravity but by vertical dispersion and the nature of the boundary condition at the sediment–water interface. Vertical dispersion, in turn, is dependent on the physical characteristics of the lake, especially depth. If different constituents interacted with suspended particulates in the same way, then apparent net settling velocities for such constituents should be the same in a given lake. This is not the case for phosphorus, plutonium, phytoplankton, and DDT because the range of apparent net settling velocities for these constituents spans an order of magnitude in both Lakes Michigan and Superior. If it is assumed, however, that a given constituent interacts with suspended particulates in the same way, in different lakes, then the ratios of apparent net settling velocities for such constituents between any two lakes should be consistent. Indeed this appears to be the case for phosphorus, plutonium, and DDT. This result further strengthens the argument that particulate settling is a major loss mechanism for DDT in the water column at the whole system scale in the Great Lakes.

An additional check on the internal consistency of the results for Lake Michigan can be made by comparing net downward DDT flux from the model results to an independent estimate of net downward DDT flux into the surficial sediment. By the principal of continuity, these fluxes should be equivalent. Net downward DDT flux is given by the product $v_s C_P$ in eq 1. Using coefficient values for case 2, setting $C_P = (1 - f)C_T$, and using the reported range of 1–10 ng/L for C_T in 1969 (*2*), we found that this flux ranges from 2.8×10^{-9} to 2.8×10^{-8} g of DDT/(cm^2 year). Net particulate flux into the surficial sediment can be approximated by (*38*)

$$F = (1 - \phi)\rho_s R \qquad (6)$$

where F = flux (mass/(area time)), ϕ = porosity (dimen-

Table IV. Percentage Contribution to Observed DDT Loss Rates in Lake Michigan

partition coeff (K_p)	degradation half-time, years	particulate settling; load, mta			degradation; load, mta			hydraulic washout; load, mta		
		0	0.40	2.0	0	0.40	2.0	0	0.40	2.0
2×10^5	5	61	66	84	35	30	14	4	4	2
	10	78	81	91	17	15	7	4	4	2
	15	84	86	93	12	10	5	4	4	2
5×10^5	5	68	72	86	28	24	12	4	4	2
	10	82	84	92	14	12	6	4	4	2
	15	86	88	94	9	8	4	4	4	2
1×10^6	5	74	78	90	21	18	9	4	4	2
	10	85	87	94	10	9	4	4	4	2
	15	88	90	95	7	6	3	4	4	2

sionless), ρ_s = density of sediment solids (mass/volume), and R = sedimentation rate (length/time). With use of values of $\phi = 0.90$, $\rho_s = 2.45$ g/cm^3, and $F = 7$ mg/(cm^2 year) for particulates in Lake Michigan (*38*), the value of R becomes 0.03 cm/year. Flux of DDT into the surficial sediment is then given by $(1 - \phi)\rho_s RC_s$, where C_s is the mass of DDT/mass of sediment solids. So that internal consistency in the calculation can be ensured, there must be compatibility between the vertical scales for the values of R and C_s. Specifically, the value of C_s must be determined in the limit as sediment depth approaches the sediment–water interface. Sediment concentrations for DDT are not available at this scale for Lake Michigan. As an estimate of the equivalent interface value, C_s can be set equal to 18.5 μg/kg, which corresponds to the reported concentration in an assumed mixed layer in the upper 2 cm (*39*). Net DDT flux into the surficial sediment then becomes 1.3×10^{-10} g of DDT/(cm^2 year).

The value for net DDT flux into the surficial sediment is an order of magnitude below the range of values for net DDT flux from the model results. However, these values differ in the expected direction, given the assumptions in determining the former flux. The sediment data for DDT show a gradient of increasing concentration toward the surface (*39*). The determination of true interface concentrations for constituents that are closely associated with sediment solids is confounded by redistribution in the upper few centimeters, probably due to bioturbation and microturbulence (*38*). Consequently, the above value for net DDT flux into the surficial sediment is likely to be an underestimate. The available data are not adequate to provide a conclusive test for the equivalence of these two fluxes.

Proportional Contribution of Individual Processes to DDT Loss Rate

Table IV contains results of component analyses of the relative contributions of each loss mechanism in the mass balance model for Lake Michigan. These analyses included the effects of variations in external loads, degradation half-times, and partition coefficients between DDT and suspended solids. Particulate settling was found to be responsible for 61–95% of the observed DDT loss rate in the lake. Degradation and hydraulic washout were found to be responsible for 3–35%, and 2–4%, respectively, of the total loss rate. Results for Lake Superior were comparable.

The range of external loads used was from 0 to 5 times the present atmospheric load to Lake Michigan. In each case, the load was held constant over the period 1969–1978. It was assumed that any residual DDT loading from atmospheric or tributary sources was contained within this range. Values used for the DDT degradation half-times and partition coefficients were consistent with the ranges

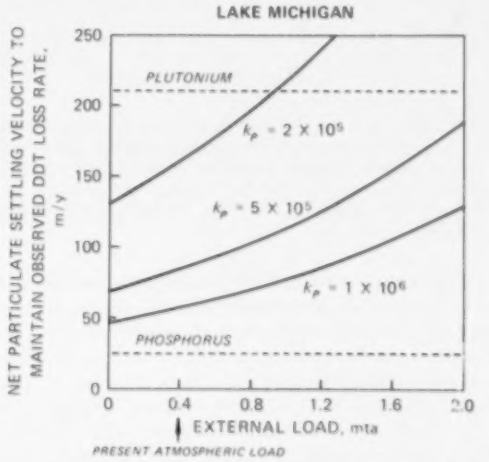

Figure 4. Results of model sensitivity analyses for net particulate DDT settling velocity as a function of partition coefficient and external load for Lake Michigan. Degradation half-time was held constant at 10 years. The dotted lines bound the range of net particulate settling velocities for Lake Michigan from independent studies (see Table III).

of reported values cited above.

Particulate DDT settling velocities for the sensitivity results presented in Table IV remained consistent with the reported velocities in Table III. Figure 4 contains an illustration of the net particulate settling velocities required to maintain the observed DDT loss rates in Lake Michigan as a function of external loads and partition coefficients, assuming the base-line degradation half-time of 10 years. The indicated upper and lower limits on the vertical axis correspond to the extremes in the range of reported velocities for the lake (Table III). For almost the entire range of sensitivity analyses conducted, the corresponding settling rates remained consistent with those found in the independent studies.

The net particulate settling velocities required to maintain observed DDT loss rates were not as sensitive to variations in degradation half-time as they were to variations in the partition coefficient. Figure 5 illustrates these net particulate settling velocities as a function of external loads and degradation half-times, by assuming the base-line partition coefficient of 5×10^5. The indicated upper and lower limits on the vertical scale have the same meaning as in Figure 4. For the entire range of sensitivity analyses conducted, the corresponding settling rates remained consistent with those found in the independent studies.

Role of DDT Vapor Phase Mass Flux

The above results contained the implicit assumption that vapor-phase mass fluxes of DDT were negligible. If

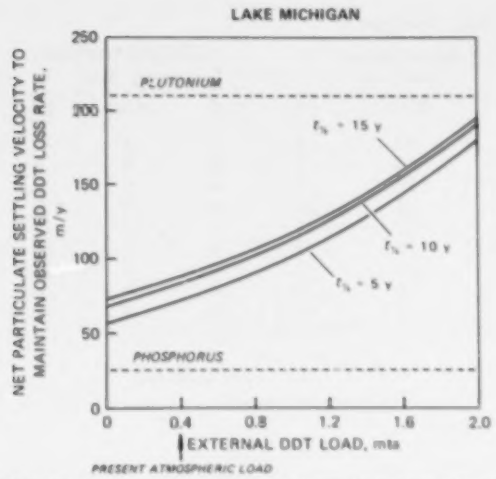

Figure 5. Results of model sensitivity analyses for net particulate DDT settling velocity as a function of degradation half-time and external load for Lake Michigan. Partition coefficient between DDT and suspended solids was held constant at 5×10^5. The dotted lines bound the range of net particulate settling velocities for Lake Michigan from independent studies (see Table III).

this assumption was not valid and there existed a significant vapor-phase mass flux from the atmosphere to the water column and, ultimately, to the sediments, then the calculated net particulate settling velocities in this study represent underestimates. This is because such a flux would have been an additional external load not included in the model. If there existed a significant flux from the sediments to the water column and, ultimately, to the atmosphere, then the calculated settling velocities represent overestimates because there would have been an additional loss process not included in the model.

Since the available data were not adequate to calculate DDT vapor-phase mass fluxes in a meaningful way, order of magnitude estimates were developed for vapor-phase gradients in an effort to draw inferences on the existence and possible direction of these fluxes. These gradients were estimated by using the fugacity approach suggested by Mackay (*40*). Fugacity is expressed in units of pressure and can be regarded as the "escaping tendency" of a constituent from a physical phase. Mass fluxes are driven by fugacity gradients, not concentration gradients, when fluxes occur between different physical phases. Mass fluxes are driven by concentration gradients only within the same phase. Fugacity bears the same relationship to mass diffusion as temperature bears to heat diffusion. Mass (or heat) diffuses from higher to lower fugacity (or temperature). The fugacity of a constituent is linearly proportional to its concentration over the range of environmental interest.

Operationally, two periods of time were defined: a preban period (ca. 1969), and a postban period (ca. 1978). These periods were somewhat arbitrary and served only to bound the period of interest in this study. All of the parameters used for the gradient calculations are contained in Table V. The methods used for calculating vapor-phase concentrations and fugacities were identical with those in Mackay et al. (*41*).

Results for the estimated DDT vapor-phase gradients are contained in Table VI. To within an order of magnitude, results were consistent with a net fugacity gradient from the atmosphere to the sediment in the preban period and no fugacity gradient between the atmosphere and sediment in the postban period. This situation is intuitively reasonable because a net mass flux to the sediment would have been expected during a period of widespread DDT use, and a zero mass flux would be expected after a sufficient period of discontinued use. With the available data, it was not possible to resolve the apparent discontinuity in the fugacity gradient in the water column during the postban period. If this discontinuity was real, it could have been caused by residual external loadings directly to the water column that were proportionally higher than the loadings directly to the atmosphere. Under such conditions, it is conceivable that local gradients and, hence, local mass fluxes, could exist between the water column and the atmosphere and/or sediment compartments.

The existence of DDT vapor-phase mass fluxes does not necessarily affect the above model results. If there was

Table V. Lake Michigan DDT Vapor-Phase Gradient Parameters

parameter	value	
vapor pressure, atm	1.33×10^{-10a}	
Henry's law constant (H), atm m³/mol	3.9×10^{-5a}	
overall liquid-phase gas-transfer coefficient (K_L), m/h	9.34×10^{-2a}	
	preban (ca. 1969)	postban (ca. 1978)
total atmospheric DDT, ng/m³	5.0[b]	0.05[b]
total water column DDT, ng/L	10.4[c]	0.512[c]
total sediment DDT, μg/kg	7[d]	7[d]
sediment bulk density, g/cm³	1.18[e]	1.18[e]
sediment fraction dry wt, g of dry/g of bulk	0.25[e]	0.25[e]

[a] Reference 48. [b] Reference 5. Vapor-phase concentration assumed to be half of total concentration. [c] Calculated from curve-fitted coregonid fish levels using $K_p = 10^5$. [d] References 6 and 39. Depth average for upper 12-cm layer. Assumed to be the same for both time periods. [e] Reference 49, for Lake Huron.

Table VI. Estimated Lake Michigan DDT Vapor-Phase Gradients

period	concn, 10^{-11} mol/m³	fugacity, 10^{-11} atm	comments
preban (ca. 1969)			
atmosphere	0.705	1.69	results consistent with a fugacity gradient from atmosphere to sediment. Possible discontinuity in fugacity gradient in water column
water column	0.294×10^4	7.64	
sediment	0.582×10^6	0.0154	
postban (ca. 1978)			
atmosphere	0.705×10^{-3}	0.0169	results consistent with no fugacity gradient between atmosphere and sediment. Possible discontinuity in fugacity gradient in water column
water column	0.145×10^3	0.377	
sediment	0.582×10^6	0.0154	

a net mass flux from the atmosphere to the sediment during the preban period and for some years beyond 1969, the effect of this extra load could have been included within the range of the loading sensitivity analyses. If there were local mass fluxes from the water column to the atmospheric and sediment compartments during the postban period and for some years prior, these fluxes would have been in opposing directions and, depending on their magnitudes, would have had self-cancelling effects on v_s in the calculations. In any case, the ambiguities of the foregoing analysis serve to emphasize the importance of acquiring the necessary data for developing more realistic mass balances of potentially volatile contaminants in the environment.

Conclusions

On the basis of trends in DDT levels in coregonid fishes, Lakes Michigan and Superior responded rapidly to the 1969 ban on DDT use. Loss rates corresponded to half-times of 2.1 years for Lake Michigan and 2.5 years for Lake Superior. These responses were more rapid than expected on the basis of hydraulic detention times and the degradation rate for DDT in the environment.

Under the assumptions in this study, settling of particulate DDT from the water column was found to be the major loss process of DDT for both lakes. Particulate settling was responsible for 61–95% of the observed DDT loss rate in Lake Michigan. Degradation and hydraulic washout were responsible for 3–35% and 2–4%, respectively. Results for Lake Superior were comparable. These ranges corresponded to results for sensitivity analyses to variations in external DDT loads, partition coefficients, and degradation half-times.

Results for apparent net particulate settling velocities for DDT were consistent with analogous results for phosphorus, phytoplankton, and plutonium from three independent studies. Detailed results for Lake Michigan showed that this consistency was maintained over a range of external DDT loads from 0 to 5 times the presently observed atmospheric load for the period 1969–1978. It was assumed that any residual DDT loading over the period was contained within this range. The net particulate settling velocities required to maintain observed DDT loss rates were more sensitive to variations in the partition coefficient between DDT and suspended solids than to variations in the degradation half-time.

The available data were not sufficient to incorporate possible DDT vapor-phase mass fluxes into the model calculations. Order of magnitude estimates were consistent with a vapor-phase mass flux of DDT from the atmosphere to the sediments during the preban period and with no significant vapor-phase mass flux between these compartments during the later years of the postban period. It was assumed that any effects of possible DDT vapor-phase mass fluxes had been implicitly included in the sensitivity analyses conducted.

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